



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of:

Yoshihito Yaginuma, et al.

Group Art Unit: 1623

Serial No.: 10/520,677

Examiner: White, Everett

Filed: January 11, 2005

For: WATER-DISPERSIBLE CELLULOSE AND PROCESS FOR  
PRODUCING THE SAME

D E C L A R A T I O N

Assistant Commissioner for Patents  
Washington, D. C. 20231

Sir:

I, Yurika Yagi, a citizen of Japan, do hereby  
declare and say that:

1. I have been employed by Asahi Kasei  
Chemicals Co., Ltd. from 1999, where I have been engaged  
in Ceolus Research and Development Department of  
Functional Additives Division of said company;

2. I have read and sufficiently understood the  
Official Action with the mailing date of June 1, 2009;  
and

3. In order to demonstrate differences  
between the present invention and US 4,483,743, the  
following experiments were conducted.

## Experimental Results

### 1. Experimenter

Yurika Yagi

### 2. Date of experiments

From January 19 to 23, 2009.

### 3. Place of experiments

Laboratory of Ceolus Research and Development Department of Functional Additives Division of Asahi Kasei Chemicals Co., Ltd., Kawashima Cho 834, Nobeoka-city, Miyazaki, Japan (〒882-0017) .

### 4. Contents and results of experiments

#### 1) Raw material

Commercially available wood pulp (Leyalpha F from Rayonier Corp., average degree of polymerization=1,821,  $\alpha$ -cellulose content=77% by weight)

#### 2) Experimental procedures

(1) The commercially available pulp was cut into 6 x 12 mm rectangles.

(2) The pulp cut was dipped into a sufficient amount of water. Thereafter, the pulp was withdrawn from the water, and the water was swished off in a sieve.

(3) The water-containing pulp cut was passed through a cutter mill ("Comitrol" Model 1700, manufactured by URSCHEL LABORATORIES, Inc., microcut head/blade distance: 2.029 mm, impeller rotation speed: 9,000 rpm).

(4) The cutter mill-treated product and water were weighed out so as to give a fiber content of 2% by weight, and the mixture was agitated until no

entanglement between fibers was observed.

(5) The aqueous dispersion thus obtained was treated with a whetstone-rotation type pulverizer ("Cerendipiter" Model MKCA6-3, manufactured by Masukou Sangyo, Co., Ltd.; grinder: MKE6-46, grinder rotation speed: 1,800 rpm). The number of the treatments was four. The grinder clearance was changed to 200 → 60 → 40 → 40  $\mu$ m, respectively.

(6) The aqueous dispersion thus obtained was passed eleven times through a high pressure homogenizer (Gaulin Model 15MR-8TA, manufactured by APV Corp., treatment pressure: 55 MPa).

### 3) Result

The aqueous dispersion thus obtained was diluted with water to make the concentration 0.1% by weight. Then, according to the method described at the present specification, the content of "component stably dispersible in water" was measured and the value measured was 15% by weight.

I hereby declare further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this            day of            , 2009.

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Yurika Yagi



0.08  $\mu\text{m}$

= 80 nm



0.02  $\mu\text{m}$

= 20 nm

1  $\mu\text{m}$



# MICROCRYSTALLINE CELLULOSE

*The oldest polymer finds new industrial uses*

O. A. BATTISTA

P. A. SMITH

From the day that the term "hydrocellulose" was first coined in 1875 until the present, treatment of cellulose with acids has been considered the wrong direction to go. By going in this direction (and making a fortunate detour) we have been rewarded with a view of an entirely new area of cellulose chemistry.

Uses of cellulose have always depended upon—and been largely limited by—its fibrous nature. In this new area, cellulose is a colloid, with all of the implied possibilities. Industrial uses are promising for:

—Flour. Nonfibrous, free flowing, absorbent, with extremely high surface area

—Compacted pellets. Hard, heat resistant, absorbent, inert

—Structural materials. Hard, insulating materials, resistant even to an oxyacetylene torch

—Gels and creams. Smooth, opaque, stable, fat-like but noncaloric

—Cellulose derivatives. Produced with greater ease and economy, and in new colloidal form

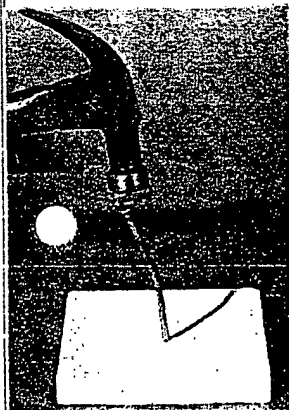
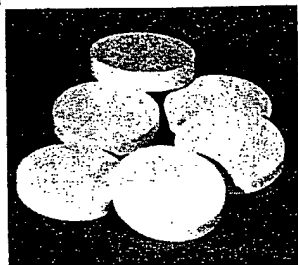
Production of the flour form is the basic step in manufacture of these types of microcrystalline cellulose. Severe acid hydrolysis removes the hinges of amorphous cellulose which link the naturally occurring microcrystals, yielding cellulose at the so-called "level-off degree of polymerization" or "D.P. cellulose." The microcrystals are freed from their fibrous, packed structure by mechanical shearing, performed in a water slurry. This is the novel step which determines the unique character of this cellulose. Drying then produces a flour of colloidal size.

The flour can be redispersed with water to form thick gels or thinner creams. It can be compacted into tablets or to large structural sheets. An entirely different, denser structural sheet results when a thick gel is dried.

**AUTHOR** O. A. Battista is the Manager of the Corporate Applied Research Department of American Viscose Corp., Marcus Hook, P. A. Smith is a Chemist in the Fiber Research Department, American Viscose.

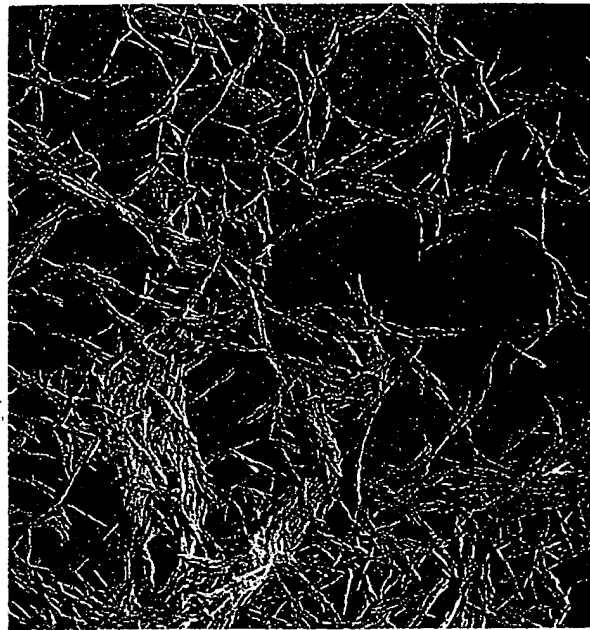
**Acknowledgment.** The authors wish to acknowledge the help of A. M. Belfort, M. M. Cruz, Jr., E. G. Fleck, Jr., C. T. Herald, and J. E. Tucker. W. A. Sisson has been especially helpful over a period of many years. F. F. Morehead provided the electron micrographs.

Appreciation is extended to F. H. Reichel, Jr., Director of Corporate Research, under whose direction microcrystalline cellulose was advanced to commercial production.

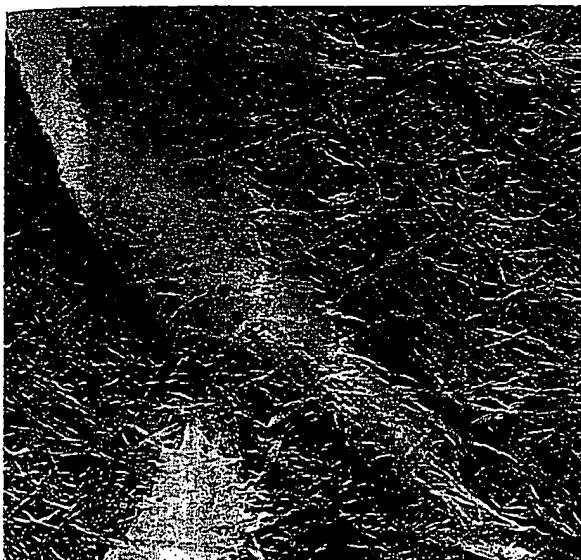




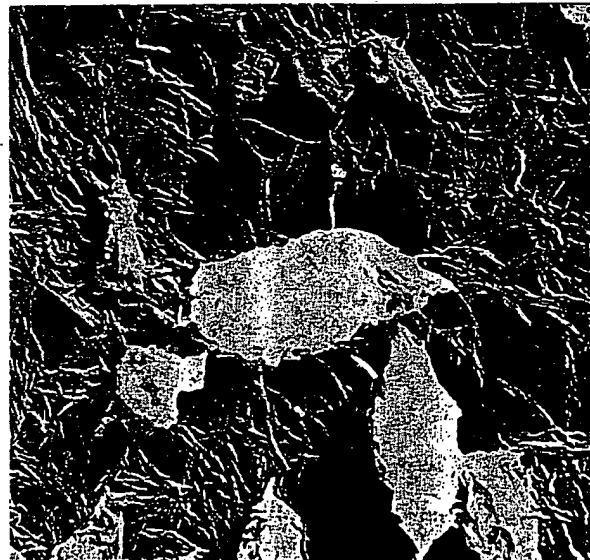
A



B



C



D

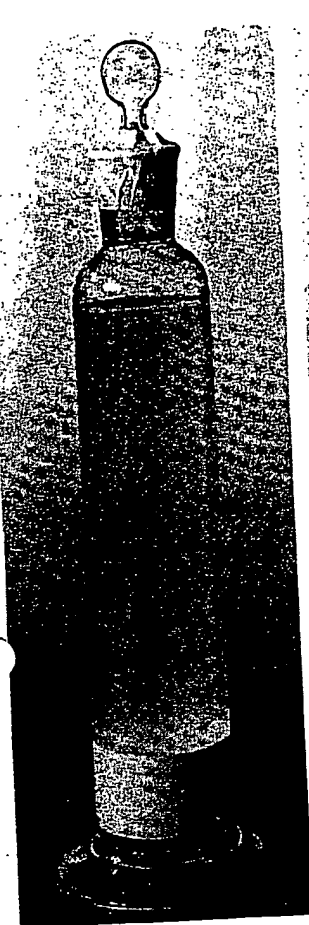
## MICROCRYSTALS OF CELLULOSE ARE BUILDING-BLOCKS

D.P. microcrystalline cellulose is capable of forming architectural patterns entirely different from any previously known structure.

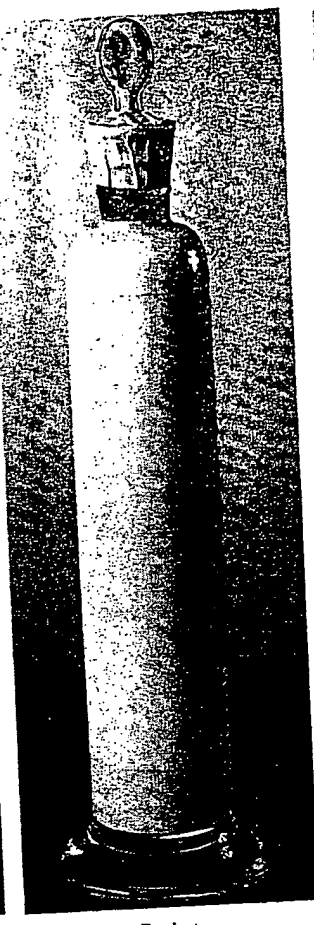
In natural cellulose the microcrystals are packed tightly in the fiber direction in a compact structure resembling bundles of wooden matchsticks placed side-by-side (A, above). Unhinging the interconnecting chains by acid treatment does not destroy this structure (B). However, the unhinged crystals are now free to be dispersed by mechanical disintegration. Figure C catches the microcrystals in the moment of peeling off the fiber. Properties of the dispersion which forms depend on how effectively they are dislodged.

An entirely new fine structure pattern appears after spray-drying (D). The microcrystals are rehydrogen bonded together, and a spongy, porous, random fine structure partly replaces the highly ordered pattern. Method of drying, initial degree of disintegration, and drying process variables all play a part in developing the inner structure of microcrystalline cellulose flour. At present, only about 20% of the unhinged microcrystals are peeled off the fiber fragments (electron micrographs at 25,000X magnification.)

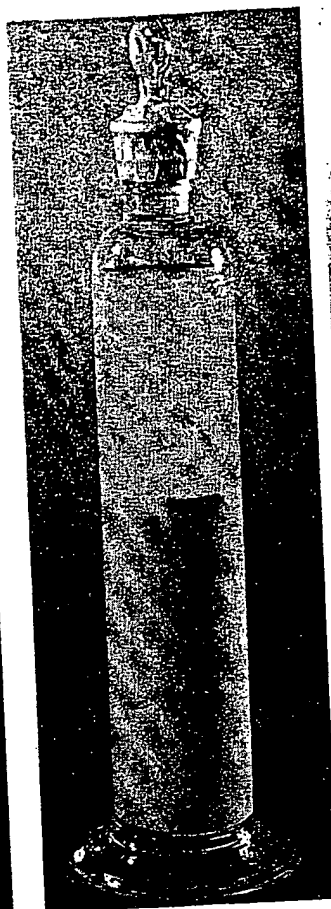
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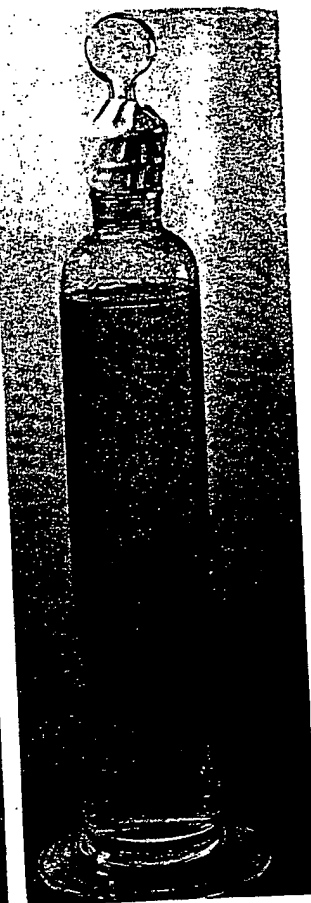
*Raw Material*



*Product*



*Pulverized fibrous alpha cellulose*



*Carboxymethylcellulose gum at 2% solids*

## THESE GELS WERE DISCOVERED WHEN AN EXPERIMENT FAILED

Several years ago we wanted to try out an idea—nucleating viscose spinning solutions with tiny, perfect, unhinged microcrystals of cellulose. We hoped to control the size, perfection, and distribution of the crystalline and amorphous regions in the regenerated cellulose structure. To produce reasonable amounts of these particles, we decided to disintegrate mechanically a concentrated water mixture of D.P. celluloses (left, above) prepared from high strength rayon tire cord. We thought that the sharp blades of a Waring Blendor would sliver off very small fragments of the agglomerated microcrystals in the D.P. cellulose. It was expected that these microcrystalline fragments would settle out of the water.

When D.P. cellulose was placed in water at approximately 5% solids, it settled out rapidly. But when this mixture was treated in a Waring Blendor at high speed for more than 15 minutes, the stable colloidal dispersion shown was obtained. The gel was opaque, snow-white, and had smooth, fatlike spreading properties.

We immediately set out to explore this new avenue, by developing uses for colloidal dispersions of microcrystalline celluloses, known commercially as Avicel (4, 7).

## DISPERSIONS OF MICROCRYSTALLINE CELLULOSE ARE UNIQUE

Pulverized fibrous cellulose, which has not been unhinged with acid, does not produce a stable dispersion. Nor do cellulosic gums resemble the new microcrystalline dispersions.

We are dealing with colloidal phenomena related largely to particle size—chemical composition plays a secondary part. The microcrystalline aggregates range in diameter from 150 to 300 A. up to about 5 microns, and are rodlike or lamellar in shape. Unlike the cellulosic gums, the ultimate unit never approaches molecular dimensions (even when diluted).

Colloidal microcrystalline dispersions share this size range with bentonite clays and colloidal alumina dispersions—and exhibit many similar properties. It is especially interesting that butter is a stable dispersion in water of fat globules of about the same dimensions. The properties of butter, such as spreadability or sheen, are related to size and size distribution of the fat globules. Some microcrystalline cellulose gels have similarly sized particles and similar functional properties.

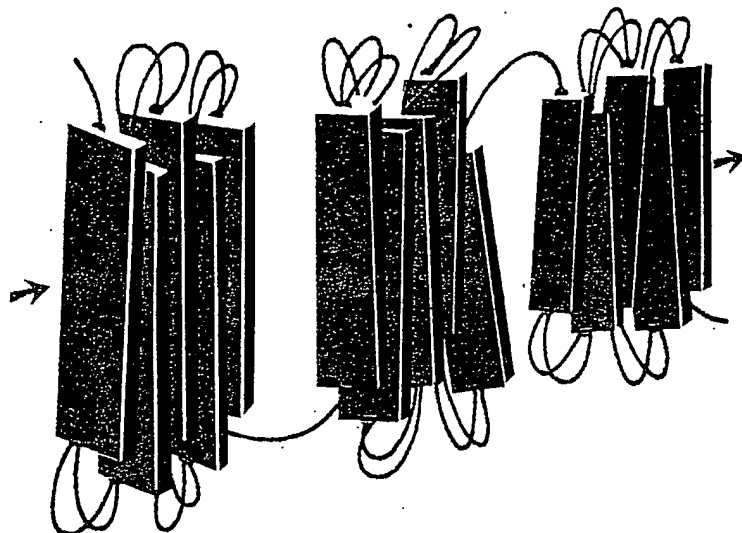
Fats and oils in many systems can now be replaced without significant change in appearance, consistency, flow properties, or spreadability.



## A Structural Model Was Developed to Explain What Happened in the Blender

Cellulose molecules form microcrystals, held together by hydrogen bonding. The individual microcrystals are linked by amorphous or disordered areas; one molecule will go through several crystalline areas. Length of the microcrystals and of the hinges is fairly constant for any particular material, depending on its history. The characteristic microfibrils have previously been shown as chains of linked crystals.

We propose this folded structure, with microcrystals packed side-by-side like matchsticks, joined by amorphous hinges. Fiber direction is shown by the arrows

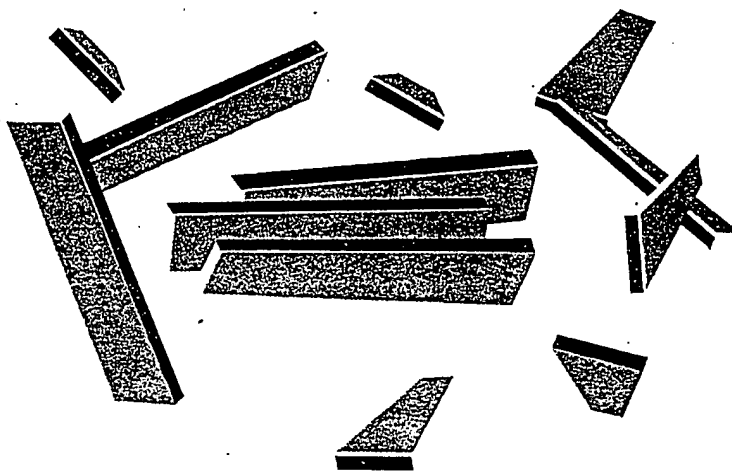


Initially, acid attacks cellulose rapidly. Mild hydrolysis breaks some of the hinges, and recrystallized areas appear. Severe acid hydrolysis breaks all of the molecular hinges and reduces the fiber to isolated crystallites

Reaction rate levels off at this stage. The microcrystals are fairly equal in size, expressed by the "level-off degree of polymerization," or "D.P." Though unhinged, the microcrystals retain their orientation in the fiber



One further step is required to produce colloidal cellulose. Mechanical agitation in a water slurry frees a fraction of the unhinged crystals. With present methods about 20% can be released. Since all of the microcrystals are unhinged, the fraction can be increased by improvement in mechanical techniques only



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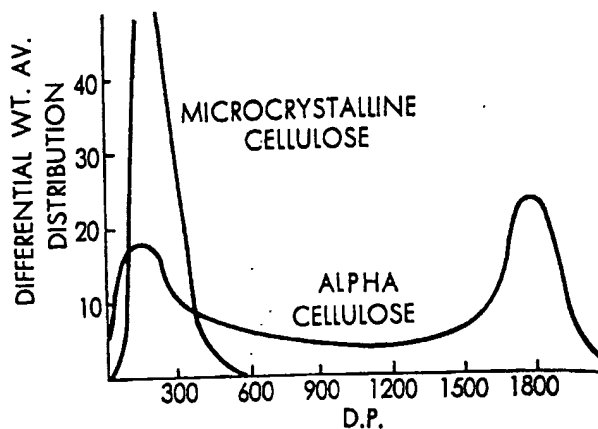
# Properties of microcrystalline cellulose can be controlled to fit end use

The unique properties of microcrystalline cellulose stem from its unique particle size and particle size distribution (see table). It is well known that reduction of almost any substance to a narrow colloidal size range can result in drastic changes in functional properties. It is important to note that by using the appropriate mechanical disintegration procedure, particle size and size distribution can be controlled. Functional properties can therefore be controlled over a wide spectrum.

Because the process for making D. P. microcrystalline cellulose breaks the molecular hinges, it results in homogenization of chain length (see figure). Avicel with the narrow molecular weight distribution shown was made from the alpha cellulose sample. (Molecular weight is 163 times the D. P.)

To avoid confusion, these definitions should be kept in mind: level-off D. P. (or D. P.) cellulose is the product resulting from, or equivalent to, the hydrolysis of purified cellulose after 15 minutes in 2.5N HCl at  $105 \pm 1^\circ \text{C}$ . D. P. varies from about 375 for bleached ramie or hemp to 15 to 25 for extra high strength rayon tire cords. It is a convenient parameter for characterizing the average length of crystalline areas in cellulose.

Microcrystalline cellulose is a mechanically disintegrated D. P. cellulose. It can be prepared from all forms of natural celluloses, alkali celluloses, regenerated celluloses, and even low D. S. cellulose derivatives. Raw material for Avicel microcrystalline cellulose is a special grade of high alpha purified wood cellulose.



Relative Size Range of Microcrystalline Cellulose Particles

Product	Appearance	Range of Diameters
Natural and synthetic gums, starches, and water soluble derivatives	Transparent or translucent aqueous dispersions	5-25 A.
Mechanically disintegrated microcrystalline cellulose	Stable opaque aqueous dispersions	150-50,000 A. (5 $\mu$ )
Pulverized fibrous celluloses	Retains fibrous form; two phases in water	40-500 $\mu$ , or higher
Microcrystalline cellulose flour	Fine white powder	Few thousand A. to over 10 $\mu$

Previous studies of treatment of cellulose with acids have had few practical or applied objectives. Most of the work has used acid degradation, with moisture regain, and electron microscopy to determine the original molecular architecture (or fine structure) of the fibrous state.

Some milestones are:

- 1875 Girard coined the term, hydrocellulose (13)
- 1925 Herzog, and Meyer and Mark postulated the crystalline nature of cellulose (15, 25)
- 1937 Staudinger and Sorkin described the dual reaction rates of acid attack (39)
- 1941 Nickerson and coworkers spearheaded the use of acid-ferrie chloride to study structure (30-32)
- 1943 Davidson demonstrated that molecular weight of cellulose drops rapidly upon initial hydrolysis, then approaches a plateau (17)
- Many others studied reaction rate phenomena and the ratio of crystalline to amorphous regions (3,5,6, 9,10,12,16-20,22-24, 26-29, 33,35-38).

- Midforties Pacsu and coworkers hypothesized a "limit hydrocellulose" which represented a rock-bottom state, resistant to acid degradation (24)
- 1947 Battista and Coppick showed that the so-called limit hydrocellulose was a reflection of crystalline to amorphous ratio, fixed by past history of the cellulose (6)
- 1950 and 1956 Battista and coworkers advanced the term, level-off degree of polymerization, and proposed a specific definition (above) (3,5)
- Average molecular weight and average length of microcrystals have been correlated (5, 23, 28)
- Crystalline nature of cellulose has been substantiated by electron microscopy and x-ray diffraction analyses (5,16,27,35,36)
- 1962 D. A. Zaukelies proposed a new schematic model for the crystalline-amorphous concept in nylons (Chem. Eng. News, p. 48, 49 (April 16, 1962)
- This article Proposes a similar folded arrangement of cellulose molecules hinging the crystalline areas and amorphous regions together (page 23). Presented before the Division of Cellulose, Wood, and Fiber Chemistry, 141st Meeting, ACS, Washington, D.C., March, 1962



## NONFIBROUS FLOUR CAN BE A CATALYST CARRIER OR A "FOOD"

Microcrystalline cellulose flour is a very pure form of cellulose, relatively free from both organic and inorganic contaminants. Its x-ray diffraction diagram shows very sharp lines, indicating an unusually high degree of crystallinity.

Density of an individual particle of the flour approaches the absolute density for a single cellulose crystal. Values from 1.539 to 1.545 were determined using a density gradient procedure.

Freeze drying produces a very light powder. Commercial production is by spray drying. Methods such as drum drying or oven drying can be and have been used. The spray-dried product, however, is an unusually fine flour with desirable physical properties.

One of the results of the spongy structure formed on drying is that microcrystalline cellulose will absorb oils and fats. Again, method of drying is important; it can cause a threefold difference in oil saturation value. Commercial product has intermediate absorption characteristics. Examples of its capacity are given opposite.

Foods are not the only application of this property. Catalysts and reactive chemicals can be applied, carried on a colloidal solid. Water-soluble dyes can be transported into oils and fatlike material without blooming. It can be an inert and edible substrate for vitamins, antibiotics, and essential oils.

Peanut butter with microcrystalline cellulose flour can be sprinkled from a shaker. A convenience in the home, this may lead to economies in the food factories of tomorrow.

The flour will convert many materials to free-flowing form when used in the amounts below.

Ingredient	Commercial Microcrystalline Cellulose, %	Ingredient	Commercial Microcrystalline Cellulose, %
Peanut butter	23.0	Maple syrup	44.0
Swiss cheese	13.8	Butter	44.8
Cheddar cheese	20.0	Lemon oil	50.0
Blue cheese	36.0	Orange oil	50.0
Plastic coconut	20.6	Corn oil	39.0
Molasses	44.0	Hydrogenated fat	39.0
Honey	44.0	Milk chocolate (melted)	32.4

### Bulk Density of the Flour Depends on Method of Drying

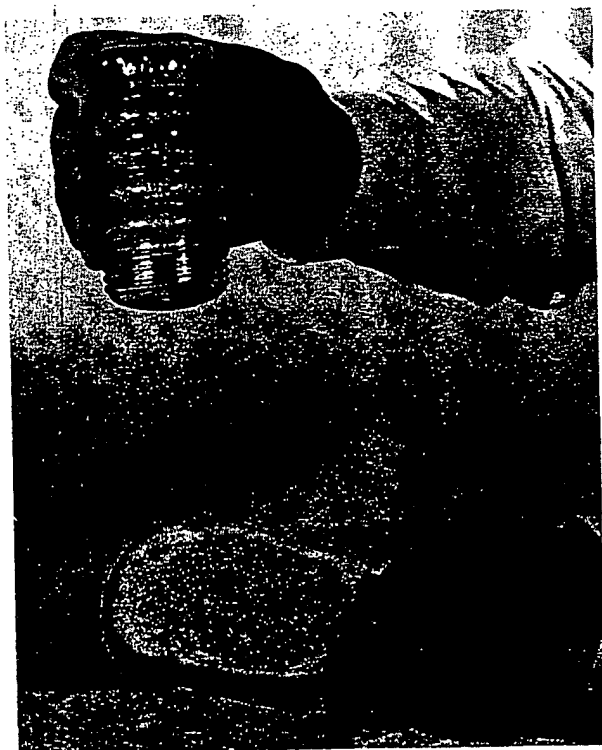
	Lb./Cu. Ft.
Freeze dried	9.8
2-Propanol-washed	13.3
Methanol-washed	14.0
Spray-dried (commercial production)	16.0-20.0

### Commercial Microcrystalline Cellulose Flour

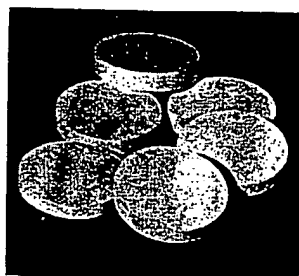
Molecular weight	30,000-50,000
Moisture, %	5
Organic solvent extractables, %	< 0.05
Ash, %	< 0.05
Calcium, p.p.m.	< 40
Chlorides, p.p.m.	< 50
Iron, p.p.m.	< 10
Copper, p.p.m.	< 4

#### Solubility

Water	Insoluble; dispersible
Dilute alkali	Partially soluble; swells
Dilute acid	Insoluble; resistant
Organic solvents	Insoluble; inert
Oils	Insoluble; inert



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## COMPRESSED FLOUR— FOR TABLETS OR FLAME- RESISTANT BOARD

A structural material so compact that it cannot be penetrated by an ordinary nail results when the flour is compressed at room temperature and 15,000 p.s.i. It has a surprising degree of resistance to an oxyacetylene torch (see table, below).

Extremely strong tablets can be formed of this material in normal tableting equipment. Catalysts, essential oils, or pharmaceuticals could still be absorbed on the tremendous internal surface of these tablets.

Compressed tablets break up immediately in liquid water, as the hydrogen bonding is destroyed. Freedom from amorphous cellulose makes them relatively insensitive to water vapor. The tablets would therefore retain their properties in a humid atmosphere, but instantly release their active components on contacting water. Water resistance can be built in by formulating with a protective resin such as an urea formaldehyde.

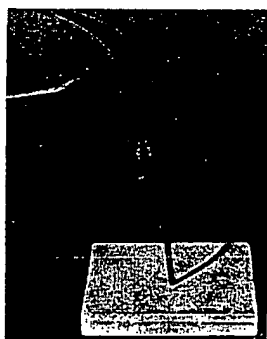
Electrical properties of the compressed powder structures are very similar to those of vulcanized fiber. With protective resin treatment, these properties can be maintained at high relative humidities.

*Moisture Pickup Is Lower Than That of Any Other Form of Cellulose*

R.H., % (71° F.)	H <sub>2</sub> O, % (After 48 Hr.)
15	2.5
45	5.7
58	6.0
81	6.2

*Compressed Flour Form of Microcrystalline D.P. Cellulose  
(Without resin treatment)*

Density, lb./cu. ft.	86-98
Specific gravity	1.26-1.34
Thermal conductivity, B.t.u./in. sq. ft. ° F. hr.	1.75
Specific heat, B.t.u./lb. ° F.	0.4
Power factor, % (58% R.H., 72° F.)	2.88
Power factor of vulcanized fiber (electrical grade), %	6.0
Dielectric constant (58% R.H., 72° F.)	5.6
Impact strength, ft.-lb./in. of notch	~ 1



## STRUCTURAL CELLULOSE— FOR HEAT SHIELDS OR "MARBLE" SLABS

An ivory-like material is produced by drying an aqueous colloidal gel of D.P. microcrystalline cellulose. Structural forms from these dried gels are generally superior in physical properties to the compressed flour forms. They are more resistant to moisture, although they will swell when in prolonged contact with liquid water (for several days). They are harder, stronger, and denser. An important difference is much better impact strength.

The electrical properties of the dried gel are almost identical with the pressed structure and with electrical grade vulcanized fiber. Method of manufacture of the new material involves only room temperature drying. Desired shapes can be molded during production. For

*Cellulose Structures Have Much Greater Heat Resistance Than Asbestos Materials*

Product	Bulk Density, Lb./Cu. Ft.	Heat Conductance, B.t.u./Sq. Ft. ° F. Hr.	Specific Heat, B.t.u./Lb. ° F.	Time under Oxyacetylene Torch, Sec. <sup>a</sup>
Compressed flour- 1/2-in. disk	86	1.80	0.4	15 (not through)
Transite, 3/8 in.	112	4.50		7 (through; melts)
Marinite, 3/8 in.	75-80			7 (through; melts)
Dried gel structure, 3/4-in. block <sup>b</sup>	~95			70 (crater depth, ~ 1/2 in.)
3/4 in.-Steel				5 (Through; melts)

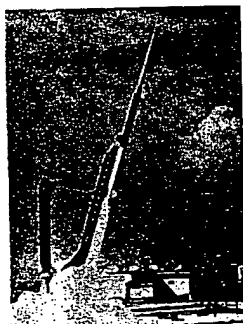
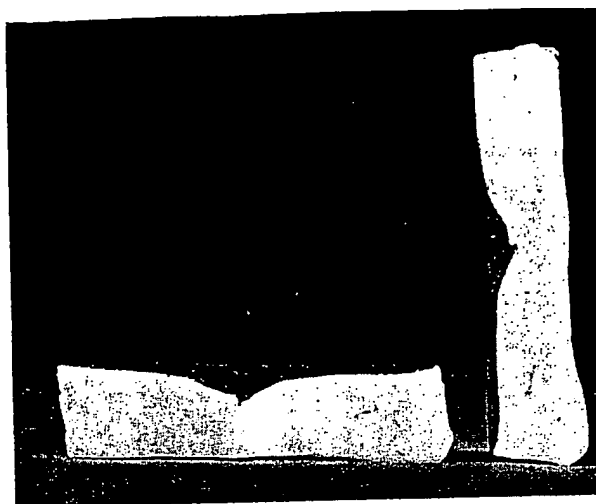
<sup>a</sup> 6600° F. <sup>b</sup> Dried from 15% microcrystalline cellulose gel.

electrical use, a material similar in electrical properties to vulcanized fiber, with some superior physical properties, can be manufactured and fabricated much more easily.

The dried gels will withstand an oxyacetylene torch three to four times longer than the compressed flour. The erosion process is most interesting—ablation involves only surface carbonization with an attendant slow erosion.

Heat conductivity is less than that of the compressed flour structure.

*The interior of this block (a dried gel structure) is completely unchanged by heat. It was subjected to an oxyacetylene torch for 30 seconds, then sawed in half. The sample could be handled almost immediately after the flame was removed, showing the very low thermal conductivity of the material*



#### DERIVATIVES OF CELLULOSE CAN BE COLLOIDAL TOO

Reaction of the microcrystalline cellulose proceeds with particular ease and speed. Derivatives can be formed which are also colloidal. These are entirely new materials with very different properties and potential applications.

At high degrees of substitution (D.S.) derivatives of microcrystalline cellulose are substantially the same material as produced from conventional cellulose. At low D.S. where the colloidal nature is maintained with surface substitution, the derivatives from colloidal dispersions. Dispersions of at least 20% solids in water can be produced. These may have the appearance of greases, ointments, or lotions, depending on the materials present.

An example of a new type of derivative, microcrystalline carboxymethylcellulose at low D.S. is shown. In dispersion at about 20% solids, this is a partly opaque nongreasy spreadable ointment with a consistency which suggests use as a suntan lotion. It does not remotely resemble the stiff conventional gel of CMC shown on page 22. The photomicrograph shows the reasons for this difference.

Other derivatives can be prepared Methyl-, ethyl-, and hydroxypropylcelluloses with unusual properties have been studied. Nitrated D.P. cellulose derivative has particularly important potential applications in solid rocket propellants; it can be readily made into a particulate form with particles in the 1-to 3-micron range. Properties of all of these materials can be con-

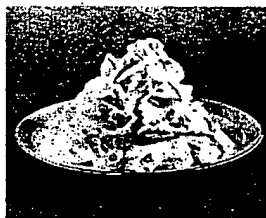


*A low D.S. carboxymethyl derivative of microcrystalline cellulose. Instead of a solution of molecular dimensions, the freed microcrystals remain substantially unchanged in size. Microfibrils of unhinged but unfreed microcrystals also are left intact*

trolled over a wide range by varying degree of substitution, the heterogeneity of this substitution, and the nature of the topochemically substituted group.

Microcrystalline D.P. celluloses in flour form exhibit an unusual affinity for hydrophobic reactants, including catalysts, which is believed to be related to the sub-microscopic porosity of the particles. Distribution of such active chemicals over such large surface areas of cellulose proffers new advantages in preparing cellulose derivatives.

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## COLLOIDAL GELS— FOR FOOD PRODUCTS OR COATINGS

Redispersion of the colloidal flour in water gives white, opaque gels or creams with functional properties which suggest many applications in a variety of industries. Some of these are:

—Gels are thixotropic and are stable over a period of years except at extreme dilution. A moldable gel is formed at about 20% solids. Dilution to 10% solids produces a pourable cream.

—The colloidal particles have an electronegative charge.

—Colloidal dispersions can be used to form extremely adherent films and coatings on glass (7). It is possible that such a coating on glass fiber would provide a cellulosic surface, adapting the fiber to normal textile weaving equipment.

—A similar extremely thin adherent film can be deposited on aluminum. Electrical capacitors could be built up, using films a few microcrystals thick.

—Gels and dispersions possess unusual compatibility with emulsions of oils and fats, as well as with sugar.

—A 15% dispersion of microcrystalline cellulose may be sterilized in a closed container for at least one hour at 240° F. without any breakdown of the stability of the gel. A viscosity increase is usually observed.

—The addition of emulsified fats or oils as well as the addition of significant amounts of sugar to a 15% colloidal dispersion of microcrystalline cellulose permits these mixtures to be deep-frozen or thawed repeatedly without significant breakdown of the gel structure and attendant syneresis. Without the presence of other components, quick freezing leads to a breakdown of the suspensions upon thawing.

—At high dilutions, they do not disperse to particles of molecular dimensions: the smallest dispersed particles are the unit microcrystals which consist of tightly packed bundles of several hundred cellulose molecules.

**Viscosity of Dispersions.** The solids concentration, at the time of the mechanical disintegration step, is a major variable in the development of the viscosity and the thixotropic properties of gels as well as stable colloidal dispersions with microcrystalline D.P. celluloses.

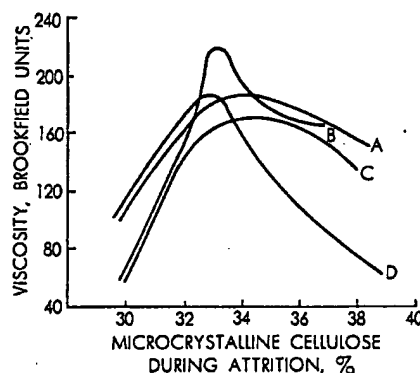
The optimum solids content to produce maximum dispersion will vary with each type of equipment used for the mechanical disintegration step. For example, 40 to 50% solids for a roll mill, 34 to 36% solids for a Hobart mixer with solid paddle, 10 to 15% for a Waring Blender or an Osterizer, and 10 to 20% for piston-type homogenizers.

As shown in the graph, viscosity of a gel depends on attrition equipment, past history of the cellulose, and concentration during attrition.

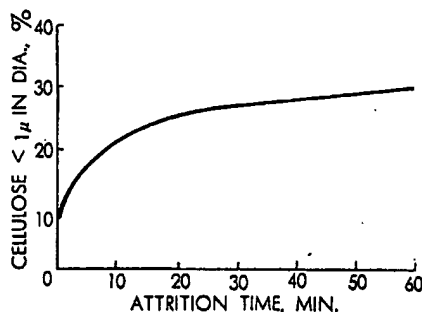
Effect of PH on Viscosity of 5% Colloidal Dispersion

pH <sup>a</sup>	A <sub>v</sub> . Apparent Viscosity <sup>b</sup>
7	8.8
8	93.4
9	118.2
10	148.8
11	61.1

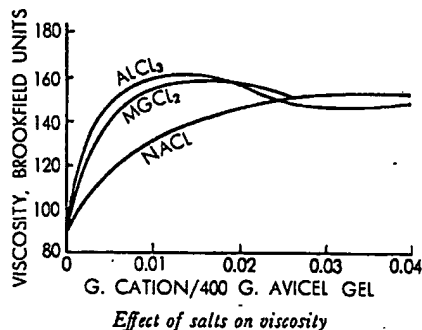
By adding NH<sub>4</sub>OH. Ostwald viscometer.



The attrition step must be performed in a rather critical concentration range. The dry flour was mixed with water under the conditions shown, and viscosities were measured after dilution to 15%. A, commercial spray-dried, Hobart, 20 min.; B, never dried, Hobart, 20 min.; C, lab. spray-dried, Hobart, 20 min.; D, commercial spray-dried, Mixer, 10 min.



Attrition develops particles of colloidal size



Effect of salts on viscosity

**Effect of Disintegration Time.** Mechanical disintegration with time develops varying amounts of true colloidal size particle aggregates that are less than 1 micron in diameter. These are the particles freed from the fiber. These particles remain in permanent suspension. It is the extent to which they are developed which controls the stability and many of the functional properties of the resulting colloidal suspensions or gels.

Microcrystalline cellulose dispersions or gels retain their colloidal stability as long as the mechanical disintegration produces a sufficient amount of the hydrated submicron particles to support a continuous gel network. Such physical properties of the gels as viscosity, stiffness, and stability are related to the particle size distribution of the gel. At the same solids content, gels prepared by means of a Waring Blendor, for example, have properties that are different from gels prepared by a laboratory Hobart mixer at higher solids content with subsequent dilution. Microscopic examination of such gels reveals major differences in the size and distribution of the visible particles.

**Effect of pH.** Data on one of the original colloidal dispersions (prepared using a Waring Blendor) show that the apparent viscosity of a 5% colloidal dispersion of

D.P. cellulose reaches a maximum at pH of about 9 to 10.

**Effect of Salts.** As might be expected, salts have varying influences on the apparent viscosity of colloidal dispersions from D.P. celluloses. Interestingly enough, if salts are present in the aqueous mixture at the time of the mechanical disintegration, the subsequent viscosity development is decreased. On the other hand, addition of salts, once the stable colloidal gel is produced, usually increases the apparent viscosity.

**Producing the Gel.** Dilution of stable colloidal dispersions of microcrystalline cellulose at high solids concentrations should be carried out gradually to reduce localized over-dilution and a tendency for the agglomeration of relatively large particles. When mechanical disintegration of microcrystalline cellulose at high solids contents is extended for a long time, or when localized over-dilution occurs, reagglomeration of some of the particles may take place in the form of spherical masses. Such reagglomerates, because they behave similar to a swollen mass of gel, are difficult to redisperse. They are receptive to breakdown by commercial homogenization equipment, however. We refer to them as rosettes because of their tendency to form rose-shaped particles.

## MICROCRYSTALLINE CELLULOSE CAN BE USED SAFELY IN FOODS AND COSMETICS

X-ray diffraction patterns of D.P. celluloses establish microcrystalline cellulose as the purest form of cellulose now available. Microcrystalline cellulose is generally recognized as safe by experts. A long history of cellulose as a vital ingredient in a host of natural foods is well recognized, and has been clinically substantiated over many years. Celery, cabbage, cereals, and many other plant and vegetable foods have varying amounts of cellulose in them. It is therefore not an additive and, as such, is not subject to the clearance provisions of the Food Additives Amendment of 1958.

Research investigations with Avicel in animals and humans were planned at an early stage in the initial development. Several phases of these programs have been completed and others are still in progress. As part of this research program a human clinical investigation has been completed (14). No adverse effects were found. Both microcrystalline and natural plant cellulose pass through the human body without evidence of breakdown.

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## ⑪ 特許公報(B2)

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発明の数 1 (全11頁)

⑭ 発明の名称 セルローズの微小繊維状物

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## ⑳ 特許請求の範囲

1 繊維状セルローズを高圧均質化装置を通過させることによりつくられ、水保持力が280%以上であり、0.5重量%の水中懸濁液に60分間放置した後の沈降量が60%以上であり、且つ60℃の1モル塩酸中での加水分解による劣化増加率がCSF値50mlに粉碎されたセルローズの少くとも2倍の値を有してなることを特徴とするセルローズの微小繊維状物。

## 発明の詳細な説明

本発明はセルローズの微小繊維状物に関する。

パルプ繊維を打砕いて表面積の大きい微小寸法の粒子を有する繊維を作ることは従来からよく知られている。数10ミクロンの直径を有するセルローズを作るために各種形式のボールミルが用いられる。実験の結果ボールミルによる粉碎工程でセルローズの化学的結合が破られることがわかった。水中でセルローズを加圧して粉碎することにより1ミクロン以下の粒子径を有する微小セルローズが得られることも知られている。セルローズ

誘導体の場合にはこれを液体窒素中で粉碎することも従来例に記載されている。ボールミルを用いて音波で粉碎することにより極微小粒子のセルローズを作る方法も知られている。このような微粉化セルローズは食物用の低カロリー添加剤として用いられ、又は調合薬の調合媒体として用いられている。これらのセルローズはさらに美容乃至化粧品産業面で調合剤や、展延剤その他の媒体として広く用いられている。

10 微粉化セルローズは一般のパルプ、繊維板、および紙パルプの製造方法において用いられている通常の方法でも作ることができる。しかしながら一般的にこれらの従来の方法ではセルローズのパルプを作るために付加的な化学処理を必要とする。例えば酸による加水分解やマーセル法により加工が必要となり、これらの処理により、生成されたセルローズパルプを化学的に変質させたり又は品質を低下させたりすることとなる。

製紙産業においては紙の生成前に繊維に加えられる微粉碎工程の回数が紙の強さに直接影響を与



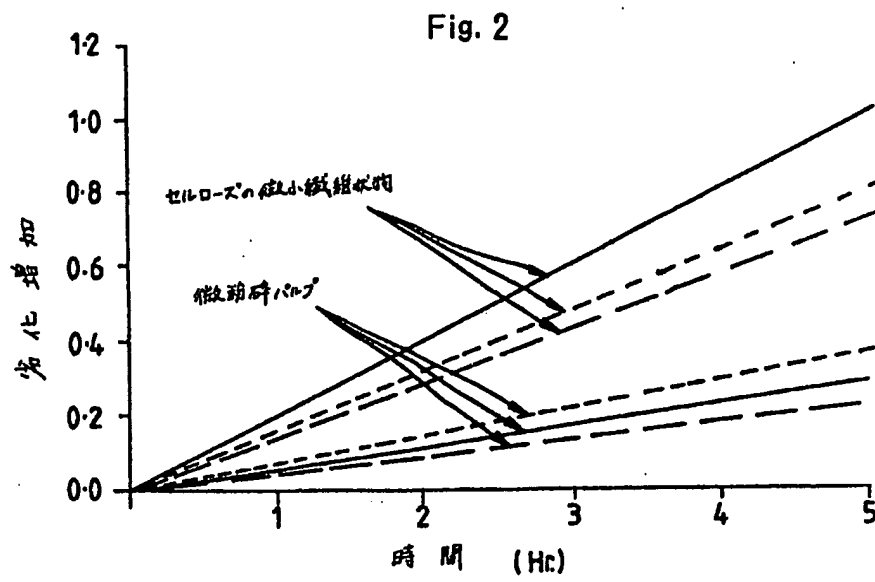


Fig. 3

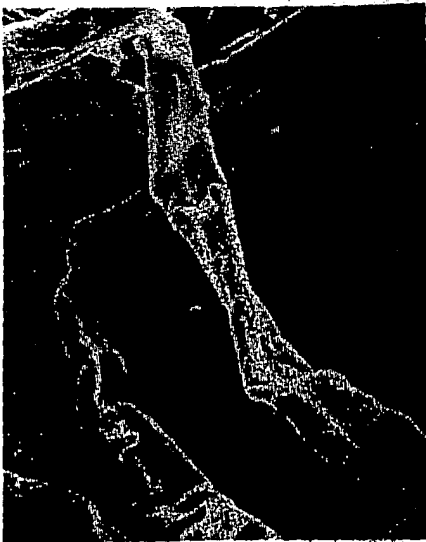


Fig. 4



Fig. 5

